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IRON-BISMUTH OXIDE DISPLAYING POTENTIAL DEPENDANT n AND p-TYPE BEHAVIOUR

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ABSTRACT

The mixed metal oxide system iron-bismuth oxide has been fabricated using atomic sputter deposition over the compositional range Fe/Bi-8 to Fe/Bi-1. Those films of composition centred around Fe/Bi-1 exhibit stable and reproducible potential dependance n and p-type semi-conducting behaviour essentially straddling the oxygen reversible potential. On the other hand, films of composition Fe/Bi-8 exhibit stable p-type photocathodic behaviour over the same potential region, a rather unusual result in that most p-type metal oxides are unstable. The former result indicates that oxides can be fabricated which can absorb and emit oxygen in the vicinity of the O_2 reversible potential. These stable films are also non-crystalline which suggest a high degree of flexibility in extending these results to other metal oxide mixtures.

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EXECUTIVE SUMMARY

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Examination of the properties of the best current metal oxide oxygen reduction electrodes suggests that they could be acting as oxygen absorbing/emitting buffers between the usually independent reactions; (i) the further chemical oxidation of the oxide by O_2 and (ii) the electrochemical reduction of this oxide. This being the case, the desirable structural and compositional properties which must be exhibited by a potentially efficient oxide based oxygen reduction electrocatalyst are the ability of the oxide to take up lattice oxygen and the presence of variable valent metal cations to provide reversibility to this oxygen uptake in the vicinity of the O_2 potential. Atomic sputter deposition is being employed with a view to producing low surface area thin metal oxide films from which intrinsic electrocatalytic activity can be readily determined and from which the semi-conductor and solid state properties can be easily obtained. In addition, we are attempting to exploit the non-equilibrium nature of atomic sputtering in order to produce stable materials not producible by normal thermodynamic growth techniques.

The mixed metal oxide system iron-bismuth oxide has been fabricated using atomic sputter deposition over the compositional range Fe/Bi-8 to Fe/Bi-1. Those films of composition centred around Fe/Bi-1 exhibit stable and reproducible potential dependant n and p-type semi-conducting behaviour essentially straddling the oxygen reversible potential. On the other hand, films of composition Fe/Bi-8 exhibit stable p-type photocathodic behaviour over the same potential region, a rather unusual result in that most p-type metal oxides are unstable. The former results, on the basis of the shape of the Mott-Schottky impedance plots and the time dependence of the n to p transition and visa versa, suggest a compositional change is responsible for the observed behavior. This indicates that oxides can be fabricated which can absorb and emit oxygen in the vicinity of the O_2 reversible potential. These stable films are also non-crystalline which suggest a high degree of flexibility in extending these results ot other metal oxide mixtures.

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TO: DR. D. MILLS
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IRON-BISMUTH OXIDE DISPLAYING POTENTIAL
DEPENDANT n AND p-TYPE BEHAVIOUR

Lynn C. Schumacher

1.0 INTRODUCTION

The design of mixed metal oxides for various electrocatalytic applications requires a more comprehensive understanding of the intrinsic properties of the mixed oxide systems and greater appreciation of the full breadth of semiconductor behaviour possible as a function of metal composition. An example is the mixed metal oxide pyrochlore structures of lead and bismuth with iridium and ruthenium which are reported to exhibit near reversible behaviour for oxygen reduction. There is virtually nothing known about the intrinsic semiconducting properties of these oxides nor an appreciation of what oxide properties may be responsible for the near reversible behaviour reported for these materials. Part of this uncertainty stems from the fact that only the electrocatalytic properties have been studied, thus the materials are studied in the high surface area form where the fabrication procedure generally has a significant impact on the solid state and surface properties.

Part of our efforts are directed toward ascertaining whether mixed oxides of the above type can be fabricated which can take up oxygen in the vicinity of the O_2 reversible potential. This is based on the premise that in order to achieve reversibility for O_2 reduction, the candidate oxide should ideally pick up lattice oxygen in the vicinity of the O_2 reversible potential with the new structure being stable at potentials positive of the O_2 reversible potential and being unstable with respect to this new oxide at potentials negative of the O_2 reversible potential. Having said this, there are two routes to be followed in exploring and exploiting the full range of possibilities inherent in this approach. In the first we are interested in oxides in which the metal species has a high cation mobility and hence can readily diffuse through the oxide to the outer oxide electrolyte interface. Ag_2O is an example of an oxide exhibiting a low overpotential for electrochemical oxidation and reduction where the cation mobility is exceptionally high. In the second route we are interested in those oxides exhibiting high oxide ion mobilities in addition to possessing a metal species (or several metal species) with an appropriate redox potential(s) in the vicinity of the O_2 potential. These oxides are generally characterized by metal cation species similar in size to the oxide ion and hence tend to dominate in establishing the crystal structure as well as (in a related way) being conducive to supporting high anion vacancy concentrations.

There are at least three classes of crystal lattices known to be moderate to excellent oxygen ion conductors. The defect fluorite structure, which can accommodate up to -25% anion vacancies is one such class while the defect pyrochlores are another/1/. O_2 reduction studies on ruthenate pyrochlore materials have, as mentioned above, resulted in performance exceeding that of platinum/3/. A number of promising combinations in this class has yet to be investigated. A third class of such materials are those having the defect perovskite structure, particularly those containing cobalt species. These materials also exhibit O_2 reduction kinetics comparable to or better than platinum. Again a number of promising combinations in this class has yet to be investigated. In an attempt to decouple the electrocatalytic behaviour from the oxygen pick-up reaction, a mixed oxide using the large cation species bismuth and the much smaller and catalytically inactive iron species has been fabricated.

2.0 EXPERIMENTAL

The metal oxides were grown by reactive co-sputter deposition from a 99.95% purity Fe target (MRC) and a 99.9% purity Bi target (Metron) both 6" diameter. Variation of the individual target voltages permitted films of variable Fe/Bi ratios to be obtained. The substrates were -4000 A thick indium tin oxide (ITO) deposited onto precleaned pyrex flats. The substrates were heated to -300°C before deposition and the mixed oxide deposited in a 100% O_2 atmosphere at -10 microns chamber pressure. After sputter deposition, the oxide films were vacuum annealed for 5 - 10 hrs at -250°C, failure to do so resulted in no detectable photoresponse. Electrodes were fabricated by gluing copper wire to uncoated ITO, and masking off the electrode with silicone sealant except for an active area of -0.3 cm^2. Photoelectrochemical measurements were made using a PAR model 170 Electrochemistry System in conjunction with a high pressure xenon lamp and monochromator.

3.0 RESULTS AND DISCUSSION

Iron-bismuth oxide of approximate surface composition Fe/Bi-8, this from Auger depth profile analysis, exhibits photocurrent behaviour characteristic of a p-type semiconductor in the potential range + 0.45 V to - 0.05 V(SCE). The photoresponse is highly stable (run for several days) in this potential region but is reversibly degraded by scanning to potentials negative of -0.05 V(SCE). Inverse capacitance plots are linear in the range + 0.35 V to 0 V(SCE) and extrapolate to a flatband potential V_{fb}^{P} = +.35 V(SCE), see Figure 1. The bandgap of this p-type oxide is indirect with E_g -2.0 eV.

Iron-bismuth oxide of approximate surface composition Fe/Bi-1 exhibits stable p-type photocurrent behaviour in the potential range + 0.45 V to -0.05 V(SCE) whereupon continued cycling to more negative potentials the photoresponse goes through zero and exhibits stable n-type behavior, decaying to zero again at -0.5 V(SCE), see Figure 2. Both the n and p-type photocurrent responses are highly stable over time as the electrodes were biased at + 0.20 V(SCE) and -0.3 V(SCE) under illumination for 24 hrs each with no decay observed, with Figure 3 illustrating this stability for several hours. Similarly, the electrodes were continuously cycled in the dark in the potential range - 0.6 V to 0.5 V(SCE) for 2 days and both types of photoresponse were subsequently unaffected. In both n and p-type regions, linear photocurrent versus normalized lamp intensity behaviour was observed indicating one electron-hole pair generated per photon

absorbed as well first order recombination kinetics. Bandgap plots of both n and p-type regions were characterized by indirect bandgaps of $E_g^{n,p} = 2.0$ eV. The sinusoidal photoresponse of Figure 2 was obtained at a scan rate of 2 mV/sec with the hysteresis being reproducible from scan to scan. At higher scan rates, > 10 mV/sec, the n to p transition could not track the change in potential. In other words, the film properties undergoing change giving rise to the change in semiconductor type is occurring on the time scale of several seconds. This can be clearly seen by scanning at rates of ≥ 20 mV/sec negative to positive, whereupon the photoresponse will remain n-type at the end potential of + 0.3 V(SCE) and then convert over several seconds to the p-type behaviour, see Figure 4. The impedance behavior of the electrode of Figure 2 is shown in Figure 5 where the inverse capacitance squared has been plotted versus potential. This plot shows very clearly the n-type behaviour in the potential range - 0.50 V to - 0.10 V(SCE) and the p-type behaviour in the region + 0.20 V to + 0.50 V(SCE). Note that the flatband potentials for both n and p-type regions agree with the photocurrent onset potentials. An estimate of the doping densities give N_d -5 x 10^{19} cm^{-3} for the n-type region and N_d -4 x 10^{19} cm^{-3} for the p-type region assuming a relative dielectric constant of k = 100. The linearity of the plot of $(I_{ph})^{1/2}$ versus V(SCE) in Figure 6, corresponding to the initially p-type phase being scanned +0.2 V to -0.15 V(SCE), suggests the transition from the p to n-type behaviour is accompanied by an excursion through a "flatband" condition, V_{fb}^{I} located in the vicinity of -0 V(SCE). Figure 7 shows the same plot but for scanning from -0.10 V to +0.20 V(SCE) giving a slightly different value for V_{fb}^{I}. This discrepancy reflects the hysteresis observed in the photocurrent behavior of Figure 2. The data of Figures 6 and 7 were obtained by scanning point by point and holding the potential at each point for ~5 minutes. Figure 8 correlates the photoresponse with the impedance plot showing the close agreement between extrapolated flatband potentials with the photoonset potentials and the breaks in the impedance behaviour with the maximum in both n and p-type photoresponses.

The cyclic voltametry (CV) behaviour of the mixed metal composition showing only stable p-type behaviour differs substantially from that of the mixture showing both n and p-type behaviour, compare Figures 9 and 10. Different electrodes of slightly differing Fe/Bi ratios but which still exhibit n and p-type behaviour showed essentially the same CV behaviour but with a further ~150 mV separation of the redox peaks observed in Figure 10. X-ray diffraction studies show these films to be noncrystalline.

The existence and stability of the material displaying both n and p-type photoresponse is in all probability related to the ability of this lattice to undergo essentially reversible compositional changes as suggested by both the cyclic voltammetry behaviour and the photoresponse behaviour. The origin of the oxidation and reduction peaks centred at 0.3 V and - 0.4 V(SCE) respectively are in all likelihood due to oxidation of Bi^{+3} to Bi^{+4}/2/. While not observed with pure Bi_2O_3, the presence of iron oxide in the lattice presumably acts to make the oxidation of Bi^{+3} easier. Iron on the other hand shows no such redox levels in this potential range and hence it is not surprising that the oxide composition Fe/Bi-8 showed no such redox peaks in this potential range. Interestingly, while iron oxide is generally n-type, it has been produced as p-type/3/ but is generally unstable as are most p-type oxides. This p-type material however is very stable in the potential range +0.5 V to 0 V(SCE). The composition which is bistable (Fe/Bi ~1) switching from p to n-type after oxidation or reduction, is

probably picking up oxygen to accommodate the presence of bismuth in the higher oxidation state in the mixed oxide. By doing so the lattice is being stabilized while the iron-bismuth oxide showing only p-type behaviour simply reduces to the metal. The time scale of several seconds for the photocurrent response suggests the uptake (and expulsion) of excess lattice oxygen occurs over a few seconds and that this change in lattice occurs around the oxygen reversible potential suggest that with an appropriate metal species in the lattice which is catalytically active for O_2 reduction, the latter may be achieved at potentials close (100-200 mV) to the reversible O_2 potential.

4.0 CONCLUSIONS

It has been demonstrated that mixed metal oxides can be designed and fabricated to exhibit to some extent properties deemed necessary for achieving reversibility as an oxygen electrode. These particular results demonstrate for the first time that a stable oxide material can be routinely switched from n to p-type (and vice-versa) as a function of potential.

The incorporation of a catalytically active metal species into this iron-bismuth matrix to form a ternary mixed oxide in an attempt to generate a reversible O_2 cathode is strongly suggested. It is unclear at present how the addition of a third component will impact on the redox and solid state behavior of the iron-bismuth oxide system.

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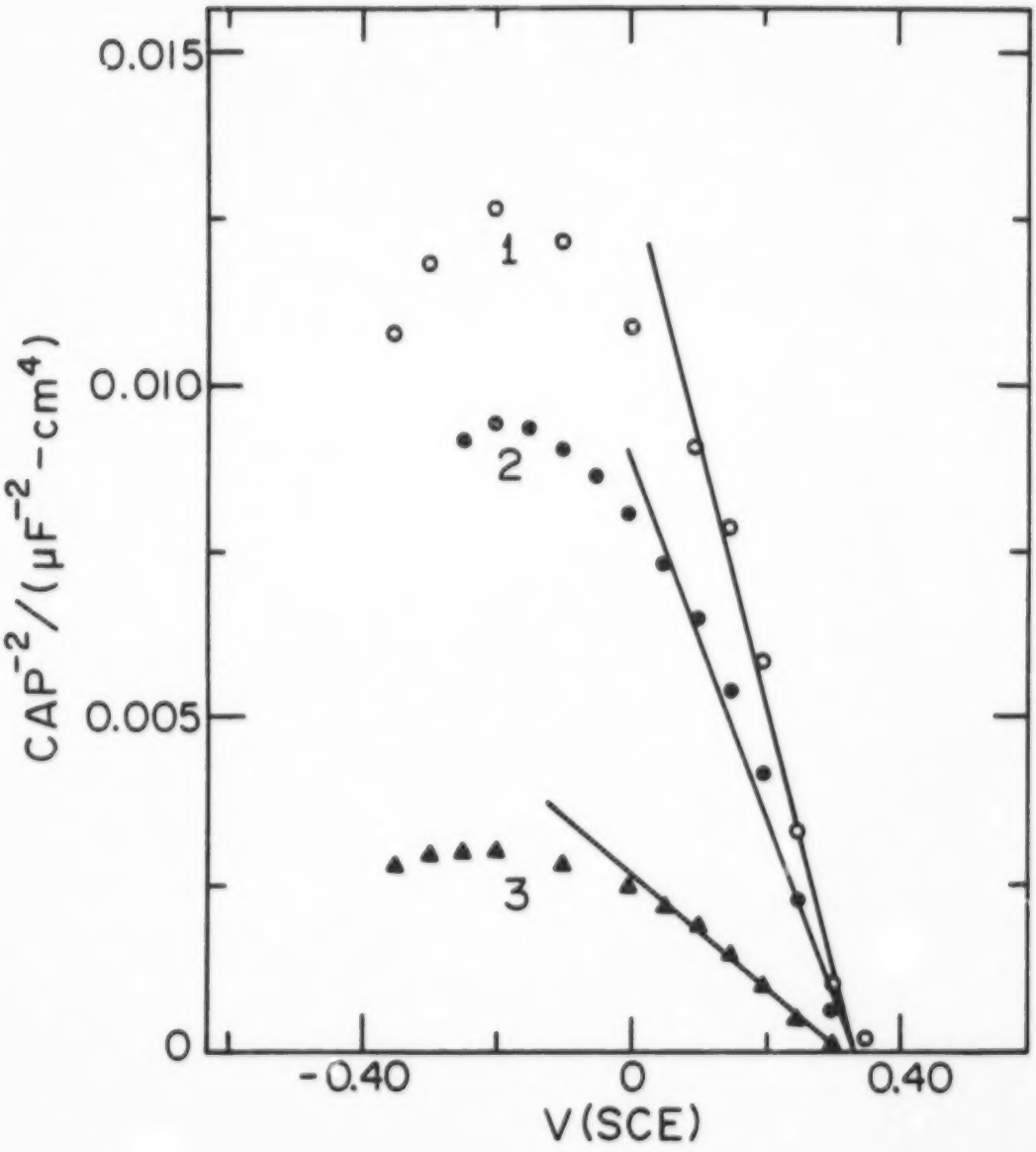

Figure 1. Inverse capacitance square plots for electrode with Fe/Bi~8 exhibiting only p-type behaviour giving a flatband potential of V_{fb} = +0.35 V(SCE).

Figure 1

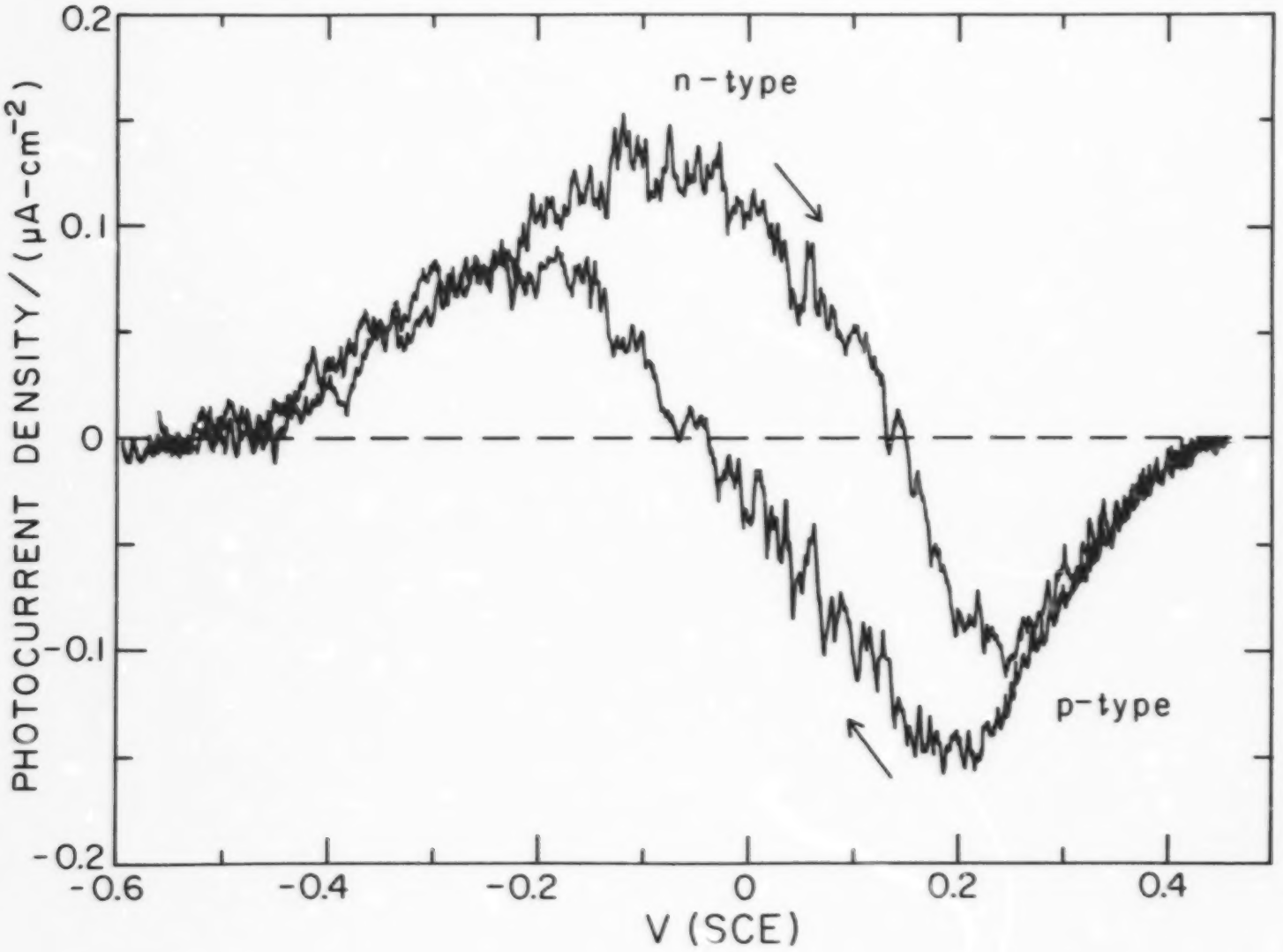

Figure 2. Photoelectrochemical response of oxide with surface ratio of Fe/Bi ~ 1 in potential range + 0.5 V to -0.6 V(SCE). Transition from n to p-type behaviour very reproducible over hundreds of scans and with different samples.

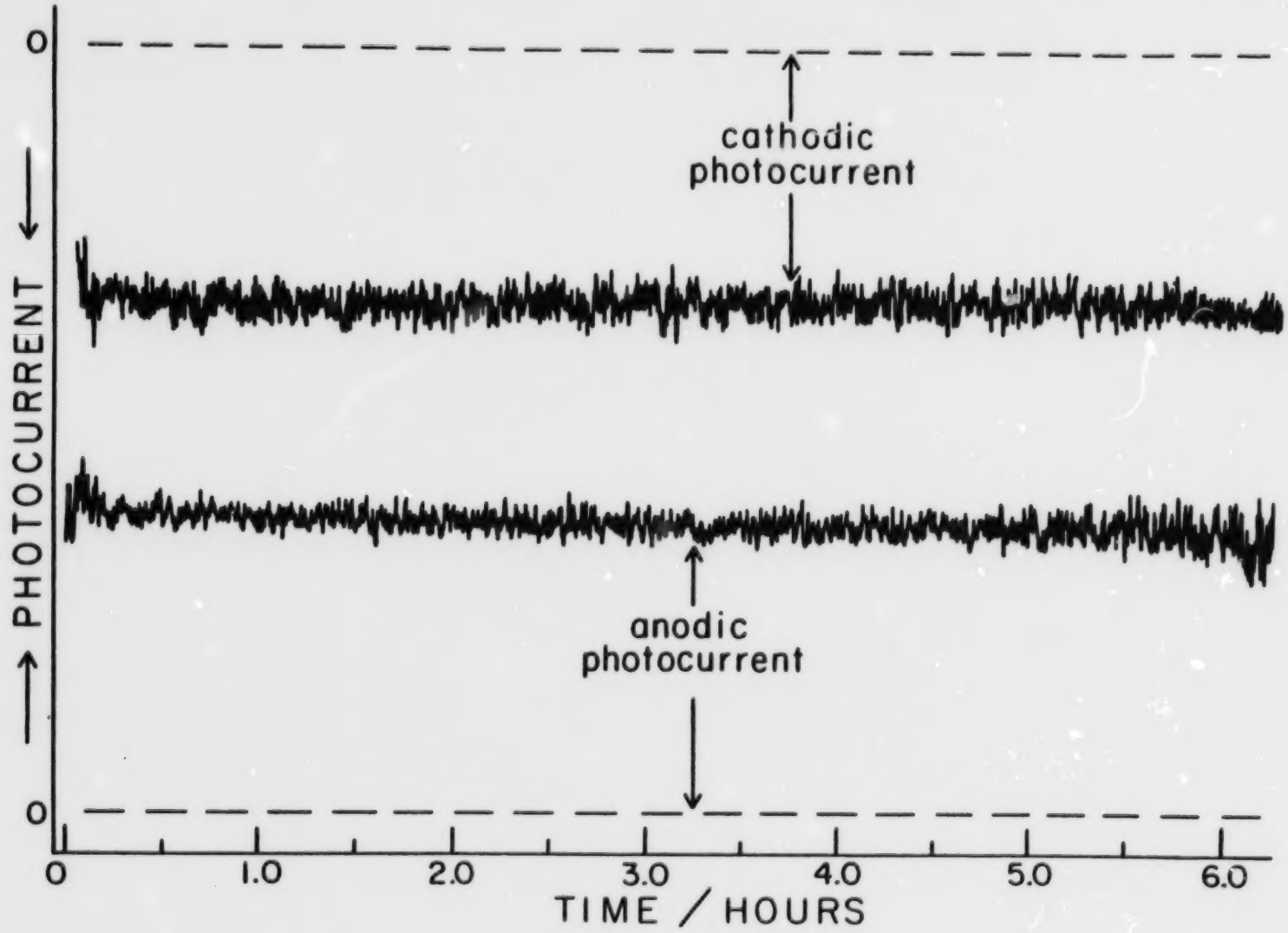

Figure 3. Time-studies of photocurrents, p-type response measured with electrode of Figure 1 biased at +0.20 V(SCE) while n-type response measured with same electrode biased at -0.10 V(SCE).

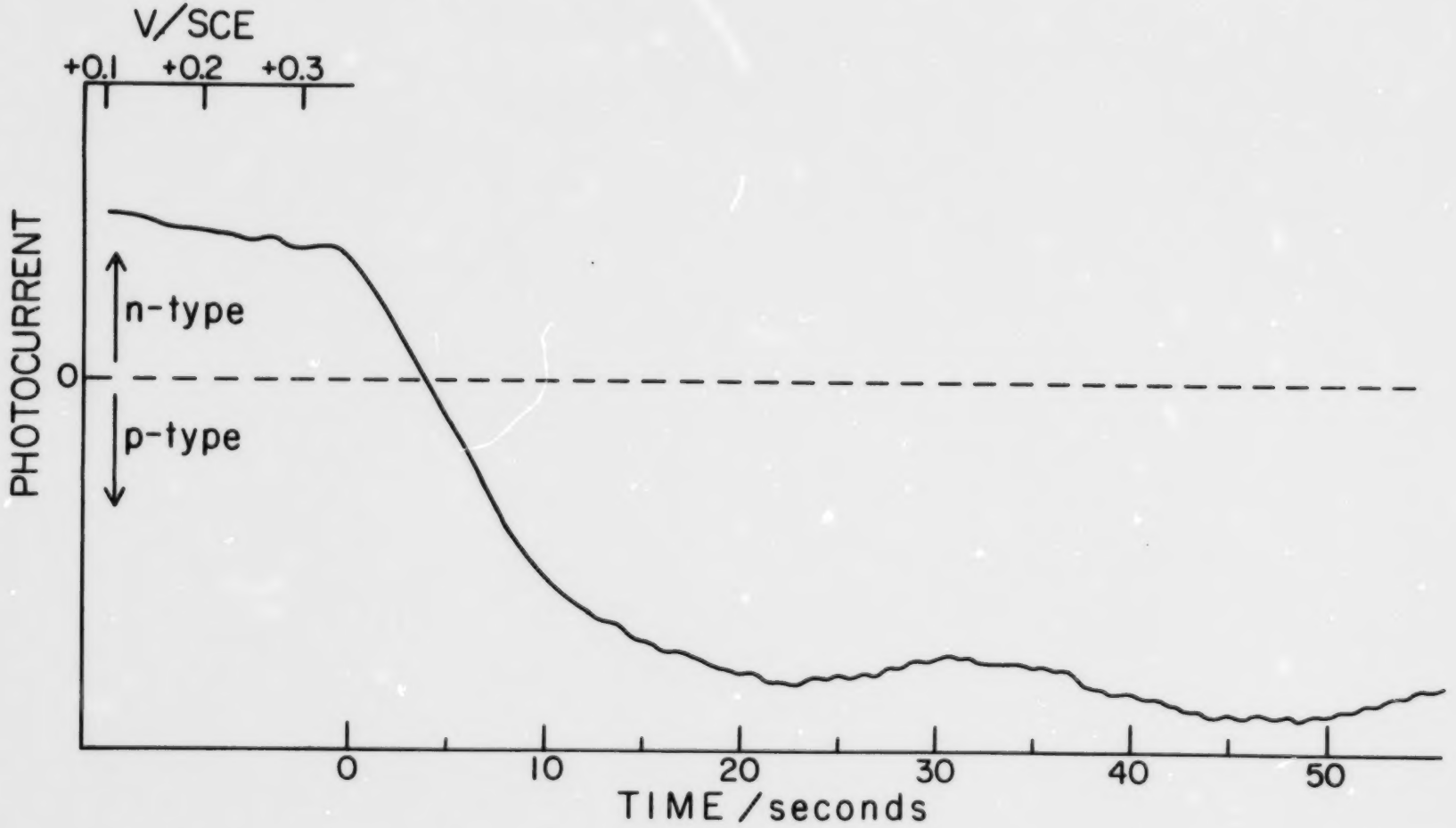

Figure 4. Time dependence of switching behavior from n to p-type where electrode was scanned at 40 mV/sec from -0.5 V(SCE) to +0.3 V(SCE) and then the photocurrent response monitored as a function of time. Similar behavior observed for switching behavior from p to n-type.

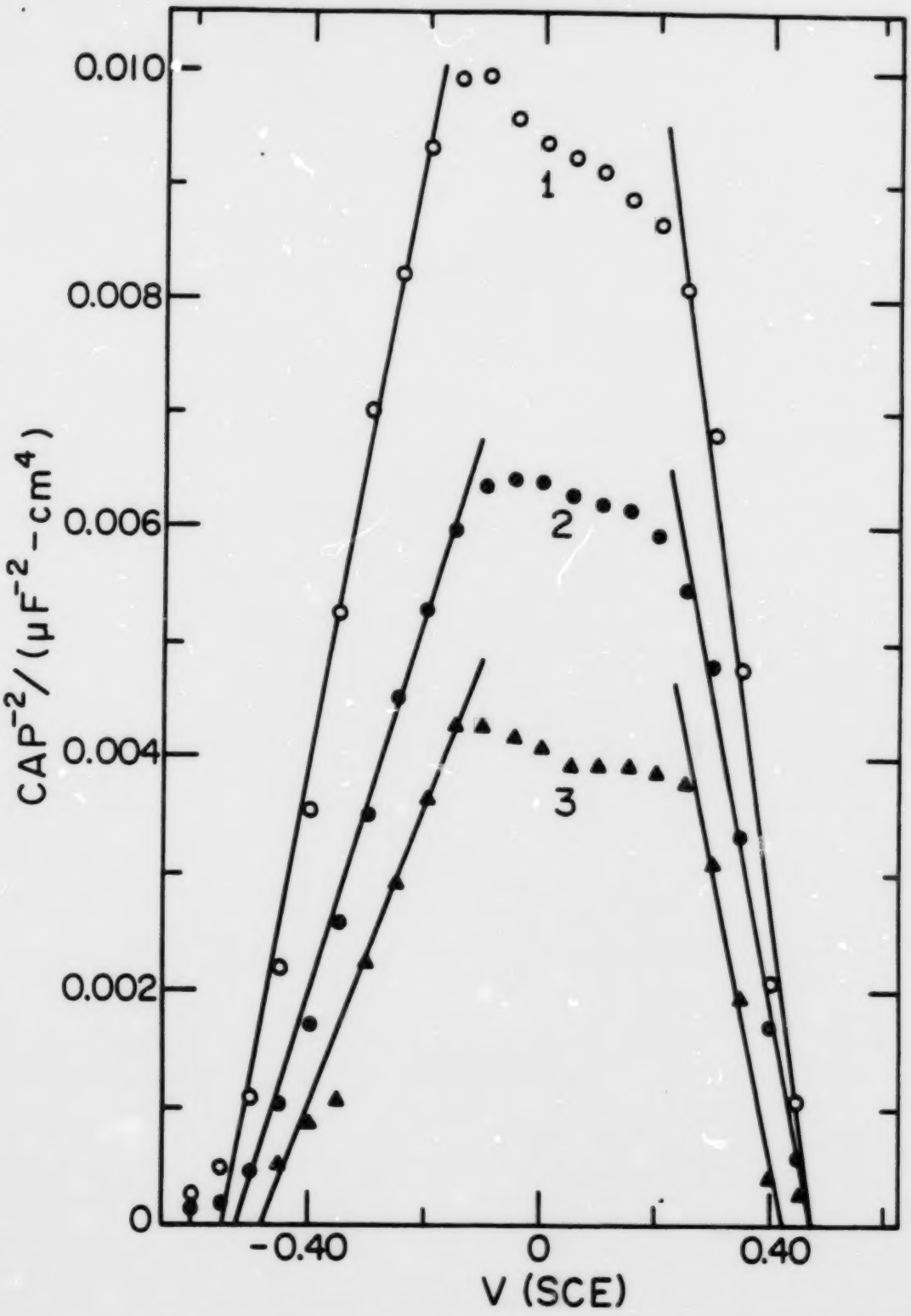

Figure 5. Inverse capacitance square plots of the electrode of Figure 2 at (1) 10^3 Hz; (20) 500 Hz and (3) 10^2 10^2 Hz, yielding on n-type flatband of $V_{fb}^{n} \tilde{=} -0.50$ V(SCE) and a p-type flatband of $V_{fb}^{p} \tilde{} +0.5$ V(SCE).

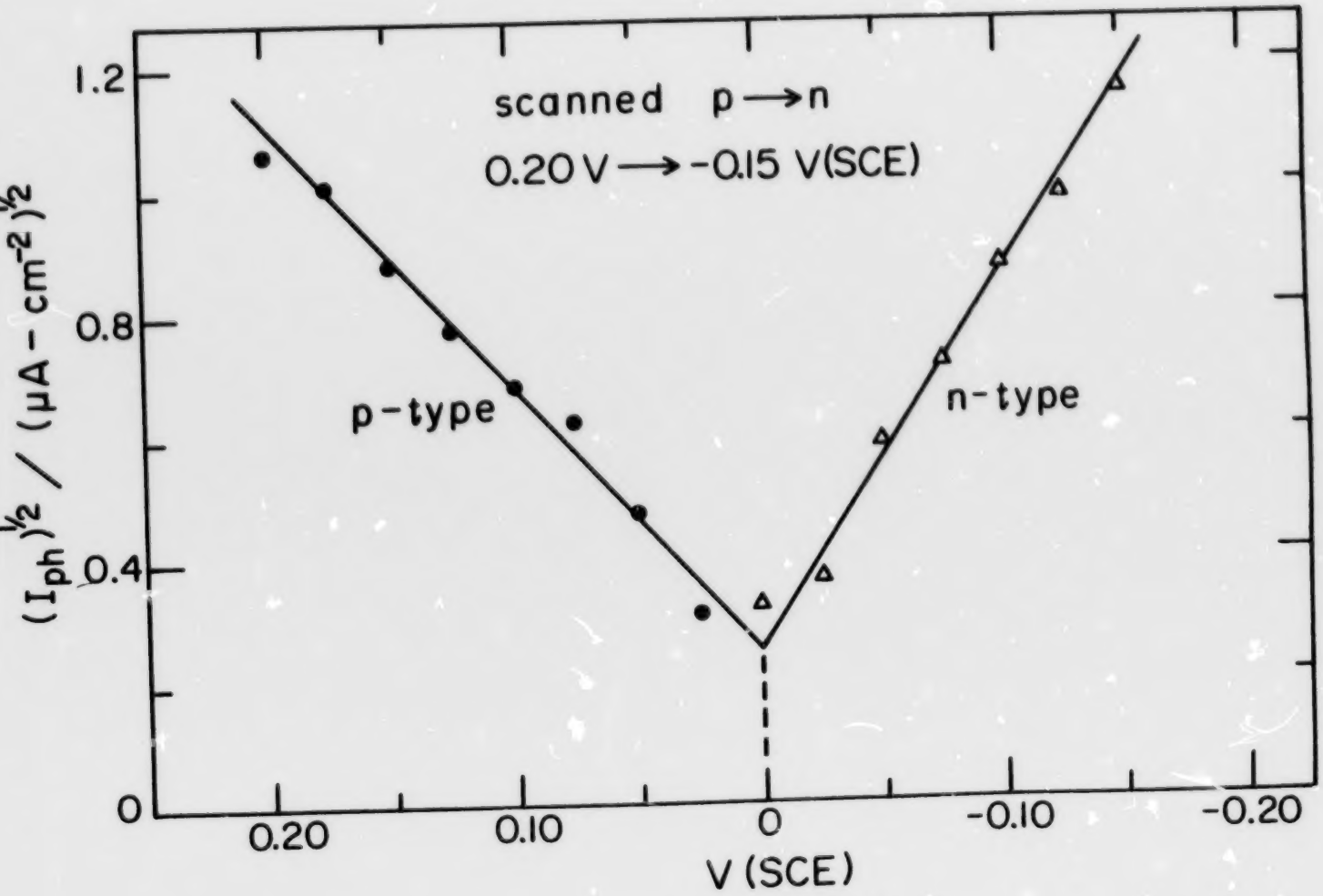

Figure 6. Plot of $(I_{ph})^{1/2}$ versus V(SCE) to yield approximate flatband at ~ 0 V(SCE) denoted in the text by V_{fb}^{I} for electrode scanned from +.20 V(SCE) to ~ -0.15V (SCE).

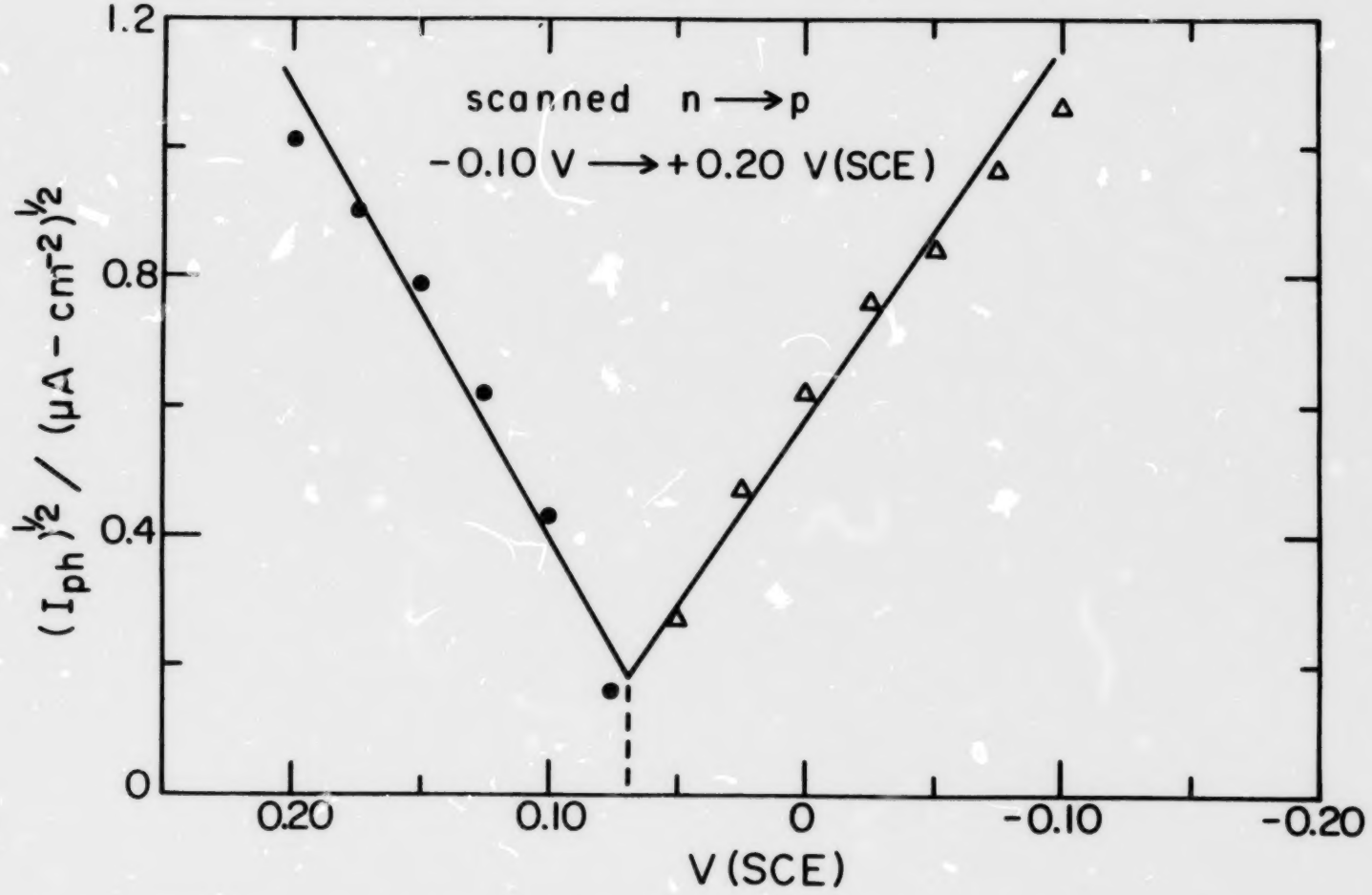

Figure 7. Same as Figure 6 but now scanned from -0.10 V(SCE) to +0.20 V(SCE).

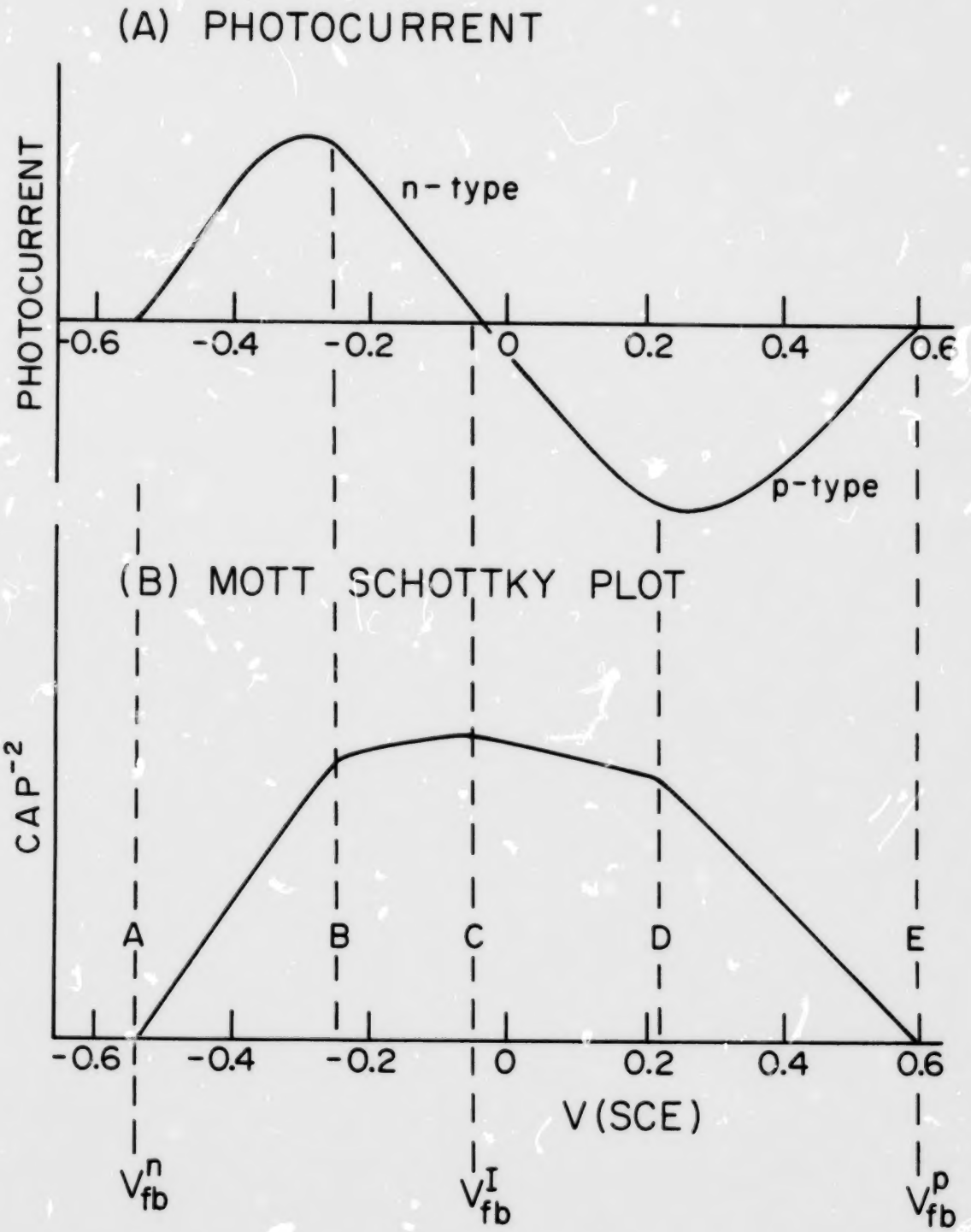

Figure 8. Correlation between inverse capacitance results and sinusoidal n and p- type photoresponse.

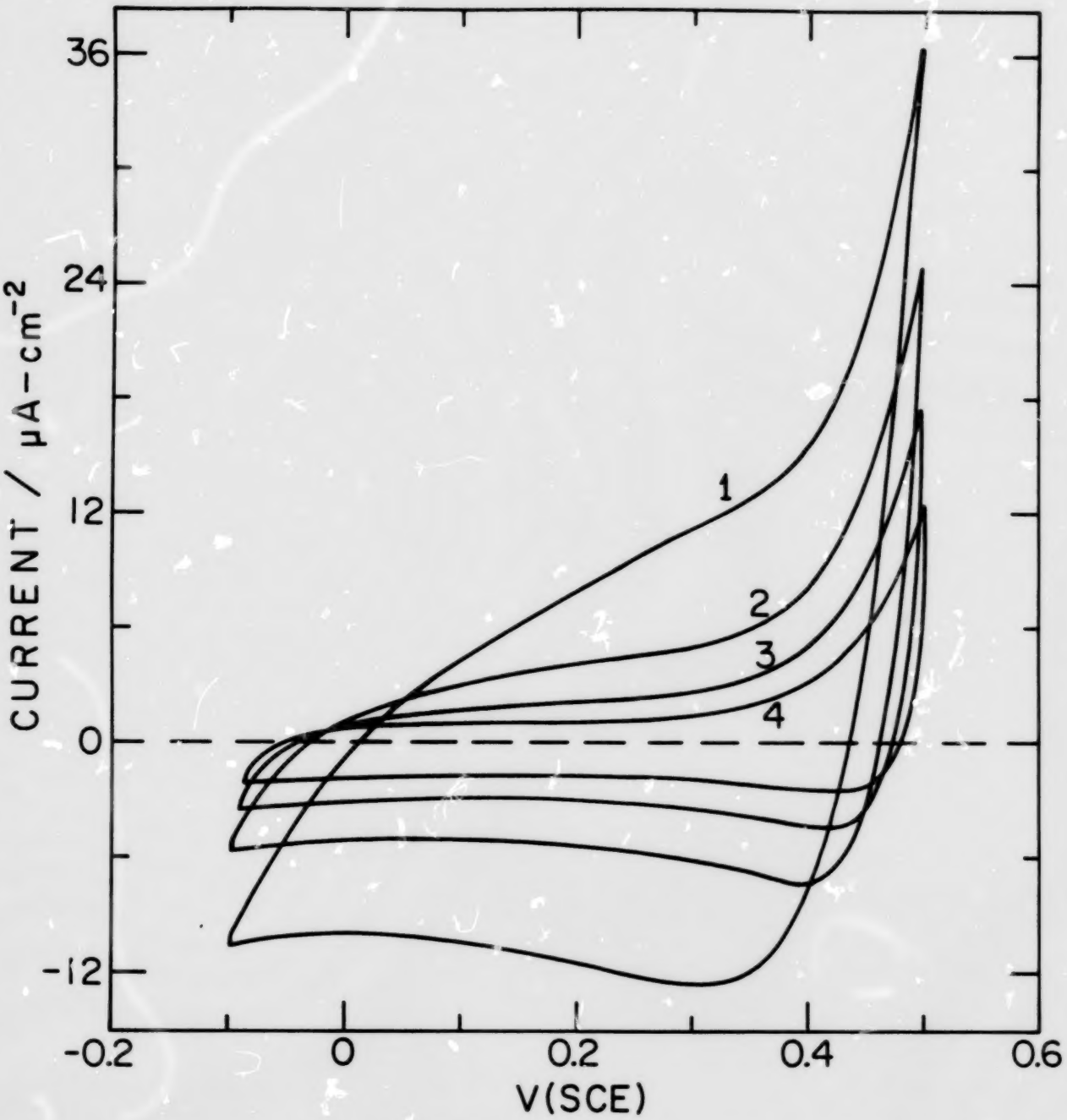

Figure 9. Cyclic voltammetry of p-type electrode with Fe/Bi=8 at: 1-50 mV/sec, 2-20 mV/sec, 3-10 mV/sec, and 4-5 mV/sec.

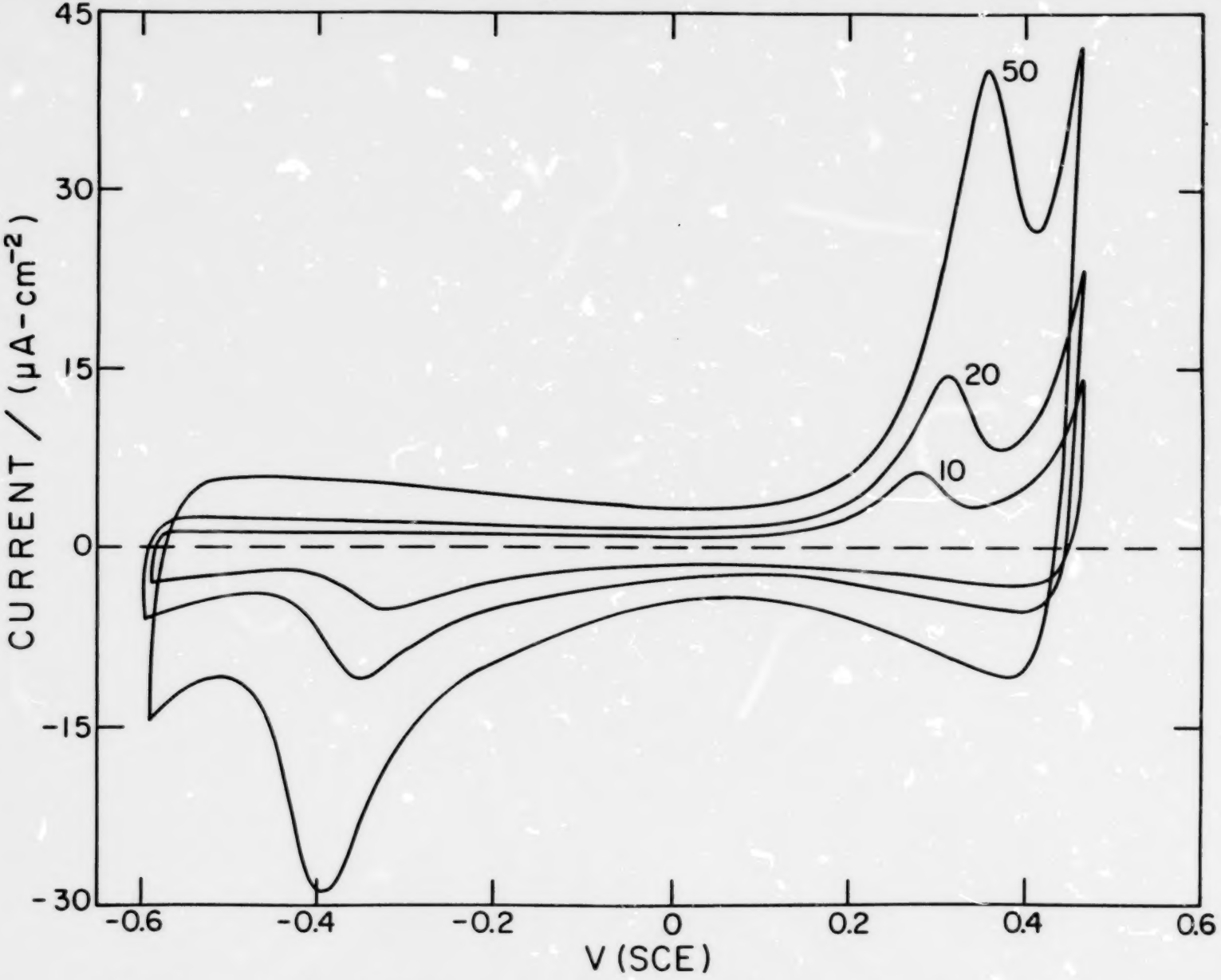

Figure 10. Cyclic voltammetry curves of bistable n and p-type oxide with Fe/Bi ~1 at several scan rates, 50, 20 and 10 mV/sec.

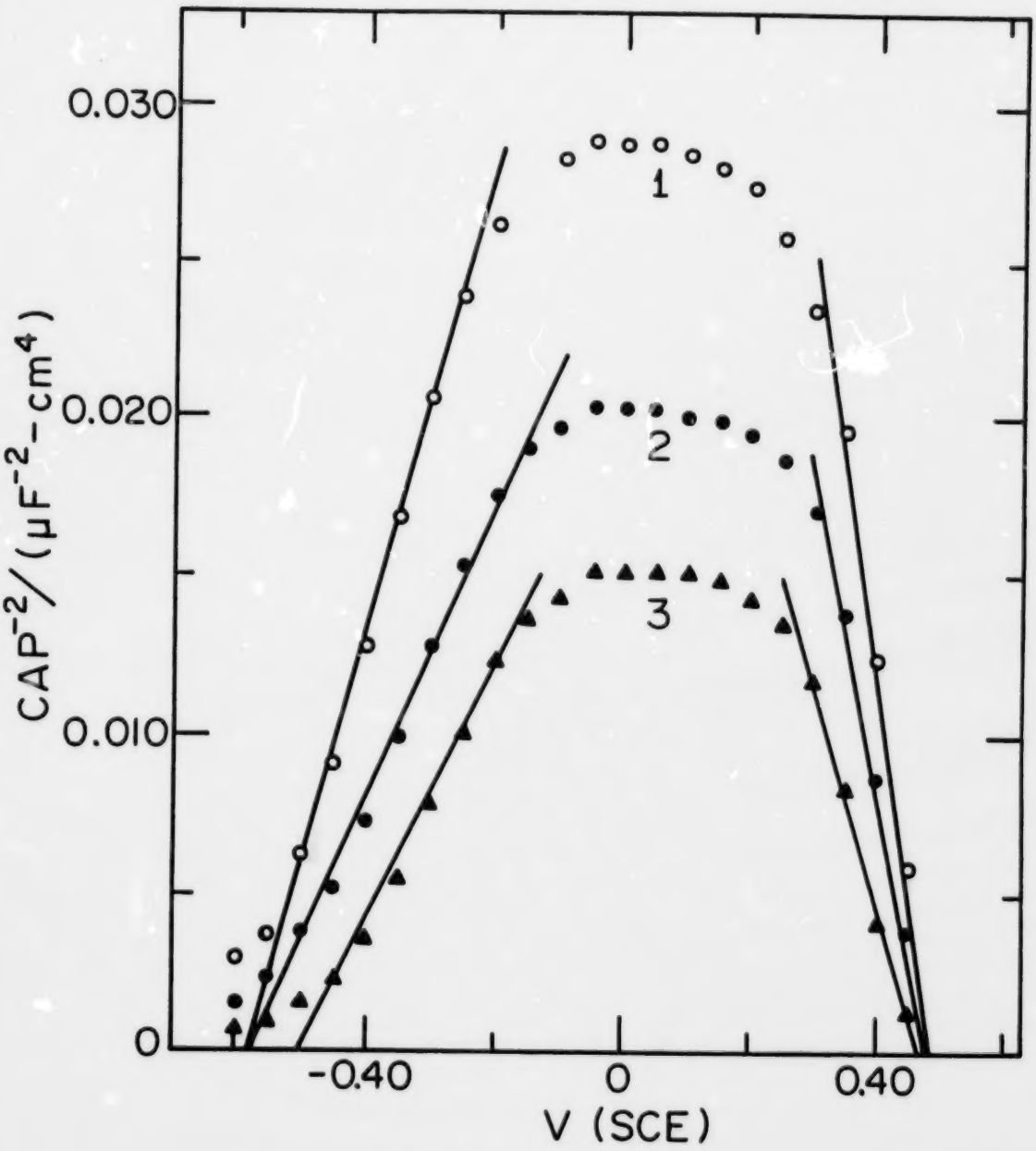

Figure 11. Inverse capacitance squared plots of another composition, Fe/Bi ~1, also displaying bistable n and p-type semiconductor properties.